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Magnetic studies on natural crystals of wolframite (Fe,Mn)WO_4

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The anisotropy and susceptibility of the naturally occuring single crystals of wolframite (Fe,Mn)WO_4 were measured over the temperature range from 90°K to 700°K. Although wolframite is a mixed crystal of Fe^{2+} and Mn^{2+} ions, the magnetic behaviour of each type could be separately obtained by assuming a perfect Curie law and magnetic isotropy for Mn^{2+} in this mixed system. The anisotropy and susceptibility due to Fe^{2+} ion only, calculated from those of the observed values of the mixed crystal were then compared with the theory worked out on the method based on Abragam & Pryce and Bose *et al.* Both the spin-orbit coupling coefficient and the effective orbital reduction factors along and perpendicular to the trigonal axis of symmetry of the ion are reduced anisotropically from its free ion value indicating anisotropic overlapping of the central charge clouds of $Fe^{2+}(3d^6)$ with *s*- and *p*-charge clouds of the surrounding oxygen ligands. Inferences have been drawn regarding the marked variation of the anisotropic ligand field with temperature.

Introduction

Wolframite [(Fe, Mn)WO_4], the chief ore of tungsten occurs in nature in the form of crystals commonly of tabular form, belonging to the monoclinic system and having perfect cleavage alonging the (010) plane. From some preliminary magnetic measurements (Spoker & Mitchell 1958) with powdered samples at room temperature only, it has been found to be highly paramagnetic. But no further investigations with single crystals and at different temperatures which are essential for understanding its paramagnetic behaviour have yet been reported. We have therefore undertaken an extensive series of measurements of the magnetic anisotropies and susceptibilities of some well developed natural crystals of wolframite over a wide range of temperature (90°K to 700°K) and the present communication gives an account of these measurements as well as a discussion of the results in the light of the existing theories (Abragam & Pryce 1951, Bose *et al* 1961, 1965).

Experimental

Samples. Good samples of single crystals were cleaved out from a specimen of wolframite obtained from the collection of Late Professor K. S. Krishnan in this Association. A chemical analysis of the sample yielded the following results :

SiO_2	—	0.68%
FeO	—	14.58%
MnO	—	9.15%
WO_3	—	75.50%

i.e., (0.614 FeO, 0 386 MnO) WO_3 as the composition of the wolframite sample, used in our investigation.

The reported structural data of wolframite (Wyckoff, 1965) as given below have also been verified here by X-rays.

Crystal system : monoclinic space group : C_{2h}^4 ($P2/c$)

Unit cell dimensions . $a = 4.82$, $b = 5\ 76$, $c = 4.97$, $\beta = 90°53'$

There are two molecules in the unit cell, one being derived from the other by reflection in the (010) plane. From X-ray data it has been found that the octahedron of six oxygen atoms surrounding each Fe^{2+} or Mn^{2+} ion, has an approximate trigonal symmetry. It is important to note here that the Mn^{2+} ion shows practically no anisotropy compared to the Fe^{2+} ion (Krishnan *et al* 1936, 1938) so that the anisotropy of the crystal may be safely treated as arising from the Fe^{2+} ion only. The mean susceptibility is contributed by both the ions according to their individual effective moments and concentration in the crystal It is however, known that the effective moment of octahedral Mn^{2+} is very close to its spin only value and obeys Curie-law very closely. Thus, as will be seen later the peculiarities in the anisotropy and susceptibility behaviours of the crystal will be mainly the features of the Fe^{2+} ion contained in it.

Measurements of Anisotropy

The magnetic anisotropy of the crystal was measured by the usual 'null deflection' method of Dutta (1956) which is a much more precise modification of the 'critical torque' method of Krishnan *et al* (1936). The crystal was first suspended with b-axis vertical. The crystal being monoclinic with $\beta \simeq 90°$ and b-axis coinciding with the principal crystalline susceptibility χ_3, we have from the measurement with this suspension

$$\Delta\chi = \chi_1 - \chi_2 \qquad \ldots \quad (1)$$

where $\Delta\chi$ is the anisotropy in the horizontal plane, (010) in this case and χ_1 and χ_2 are the maximum and minimum principal crystalline susceptibilities, respectively, in this plane. The sample crystal was in the form of an approximately circular disc, the plane of the disc being parallel to (010) plane. With such a sample a-axis or c-axis could not be recognised in the a– c plane and hence the usual procedure could not be adopted for further measurement of anisotropy with some other known axis vertical. Hence we adopted the following procedure. An arbitrary line was marked on the sample disc and its orientation with respect to x_1 axis was noted (at different temperatures) during measurements with b-axis vertical (see Datta 1956).

The crystal was then suspended with this arbitrary line in the a—c plane vertical The crystal was found to set with b-axis perpendicular to the magnetic field. From measurements with this suspension we obtain

$$\Delta\chi = (\chi_1-\chi_3)-(\chi_1-\chi_2)\cos^2\theta \qquad \ldots (2)$$

where θ is the angle between the arbitrary line and χ_1 direction.

Principal Ionic Anisotropies

From the above values of crystalline anisotropies the principal ionic anisotropy (which as already mentioned refers to the Fe^{2+} ion) can be obtained as follows .

$$K_{\parallel}-K_{\perp} = 2(\chi_1-\chi_2)-(\chi_1-\chi_3) \quad \text{when} \quad K_{\parallel} < K_{\perp} \qquad \ldots (3)$$

or $$K_{\perp}-K_{\parallel} = (\chi_1-\chi_2)+(\chi_1-\chi_3) \quad \text{when} \quad K_{\perp} < K_{\parallel} \qquad \ldots (4)$$

where K is the principal ionic susceptibility along the trigonal axis of the $Fe^{2+}O_6$ cluster and $K_{\perp}$ is that perpendicular to that axis.

$$\left.\begin{aligned} &\text{Also,} \quad \cos 2\phi = \frac{\chi_1-\chi_3}{K_{\parallel}-K_{\perp}} \quad \text{when} \quad K_{\parallel} > K_{\perp} \\ &\text{and} \quad \cos 2\phi = \frac{(\chi_1-\chi_2)-(\chi_1-\chi_3)}{K_{\perp}-K_{\parallel}} \quad \text{when} \quad K_{\parallel} < K_{\perp} \end{aligned}\right\} \qquad \ldots (5)$$

where 2ϕ is the angle between the symmetry axes of two magnetically inequivalent ions in the unit cell. The sign of $|K_{\parallel}-K_{\perp}|$ can be determined from epr results or in some cases from magnetic anisotropies. Thus our magnetic investigation unambigously shows that $K_{\perp} > K_{\parallel}$, the other alternative $K_{\parallel} > K_{\perp}$ leading to an absurd value of $\cos 2\phi > 1$. This peculiarity of the ionic magnetic ellipsoid is common to many ferrous salts (Guha Thakurta *et al* 1966).

Measurements of Susceptibility

We have measured the mean susceptibility $\bar{\chi}$ with powdered samples of wolframite For this purpose the crystals were finely powdered in an agate mortar and tightly packed in a quartz container. The container was suspended in between the poles of an electromagnet from one end of the beam of a sensitive jewel-pivoted microbalance (Das, 1963) and the susceptibility was measured in the manner already described by her. The values are corrected as usual for diamagnetism.

Measurements at different Temperatures

For low temperature measurement of $\Delta\chi$'s and $\bar{\chi}$, the specimens were kept suspended in the experimental chamber of a gas-flow type of cryostat (Bose 1947),

the temperatures being recorded by a calibrated copper-constantan thermo-couple. For high temperature measurements the specimens were suspended in a tubular electric furnace with non-inductive windings, the temperature being recorded by a calibrated chromel-alumel thermo-couple.

Table 1. Anisotropy and susceptibility of (Fe, Mn)WO_4

Temp. in °K	θ	$(\chi_1-\chi_2)$ $\times 10^6$	$(\chi_1-\chi_3)$ $\times 10^6$	$(K_\perp - K_\parallel)$ $\times 10^6$	2ϕ	$\chi \times 10$
90	26°6′	5970	6930	12900	94°16′	41098
100	26°18′	5016	5924	10940	94°46′	36932
150	27°42′	2748	3352	6100	95°41′	24722
200	27°7′	1855	2295	4150	96°5′	18622
250	30°24′	1370	1710	3080	96°22′	14932
300	31°42′	1076	1354	2430	96°33′	12480
350	33°00′	827	1048	1875	96°53′	10693
400	34°24′	640	815	1455	96°56′	9399
450	35°42′	505	645	1150	97°0′	8376
500	37°00′	381	491	872	97°12′	7548
550	38°12′	293	377	670	97°18′	6886
600	39°24′	211 5	273.5	485	97°24′	6273
650	40°30′	161	209	370	97°27′	5793
700	41°36′	116	149	265	97°29′	5361

Theory of the Ligand Field of Wolframite

Wolframite is a mixed crystal of $FeWO_4$ and $MnWO_4$. The Fe^{2+} or Mn^{2+} ion is surrounded by six oxygens forming a slightly trigonally distorted octahedron. Now, FeO or MnO single crystals are antiferromagnetic, the Neel temperature being 198°K and 122°K, respectively (Bizette 1956). But in wolframite within the range of our experiment (700°K to 90°K), no antiferromagnetic behaviour was observed. This is apparently due to the fact that the distance between Fe^{2+}—Fe^{2+} or Mn^{2+}—Mn^{2+} is much greater here because of the presence of intervening diamagnetic tungsten atoms so that the exchange interaction is comparatively much weaker. Moreover, Fe^{2+} being in D state and Mn^{2+} in S state, any antiferromagnetic exchange between them, if present, will be also very weak. It is to be noted that the observed magnetic behaviour of the substance does not favour the strong field scheme, since $Fe^{2+}(3d^6)$ becomes diamagnetic and $Mn^{2+}(3d^5)$ becomes single spin system under this scheme. The very large observed value about 5.477 BM for effective magnetic moment of the combined system at room temperature definitely precludes this possibility. We should therefore treat the crystal field behaviour of the system under the usual weak field scheme.

Since $Mn^{2+}(3d^5)$ is an S state ion, its anisotropy will be negligible ($\sim 0.1\%$ of the mean susceptibility, Krishnan & Banerji 1936). So the observed anisotropy

may be regarded as due to Fe^{2+} alone. Again the susceptibility of S-state Mn^{2+} will follow very closely the Curie's law (Van Vleck & Penney 1934), having effective magnetic moment 5.916 BM. Hence, subtracting the susceptibility of Mn^{2+} from the observed susceptibility of the crystal (with due consideration of the percentage composition) we get that of Fe^{2+} only The ligand field having no effect on the Mn^{2+} ion to a high approximation, the susceptibility and anisotropy obtained for Fe^{2+} only are then treated with the ligand field theory of Fe^{2+} ion.

Theory of the Ligand Field in Fe^{2+} Ion

From X-ray data, it is found that the Fe^{2+} ion is under a predominant cubic field with a small superimposed trigonal component. Under the predominant cubic component of the ligand field, the five-fold orbital degeneracy of the ground state $3d^6\ {}^5D$ of Fe^{2+} ion in the free state is split up into an orbital doublet ${}^5E_{2g}$ and a triplet ${}^5T_{2g}$, the triplet lying lower.

In calculating the energy levels of Fe^{2+} complex we employ the technique of Abragam & Pryce (1951) in treating the ${}^5T_2$ state as an effective ${}^5P$ state with a fictitious orbital angular momentum quantum number $l' = 1$ and effective Lande factors $-\alpha_{\|}$, $-\alpha_{\perp}$($\|$, $\perp$ to the trigonal axis), and then apply the trigonal component of the field (V_t) and spin orbit ($\zeta L.\ S$) perturbations $[-\alpha_{\|}\zeta_{\|}L_z'S_z - \alpha_{\perp}\zeta_{\perp}(L_x'S_x+L_y'S_y)]$ together. The effect of admixture of the upper ${}^5E_2$ state enters through $\alpha_{\|}$, $\alpha_{\perp}$.

The finite structure energy levels arising out of the splitting of the cubic orbital triplet ${}^5T_{2g}$ under the combined action of the axial component of the ligand field and the spin-orbit interaction are given by (Bose & Rai, 1965)

$$E_0 = \tfrac{1}{2}[(\alpha_{\|}\zeta_{\|}+\Delta)-\{(\alpha_{\|}\zeta_{\|}-\Delta)^2+24\alpha_{\perp}^2\zeta_{\perp}^2\}^{\frac{1}{2}}]$$
$$E_1 = \alpha_{\|}\zeta_{\|}x_1$$
$$E_2 = \tfrac{1}{2}[(\Delta-\alpha_{\|}\zeta_{\|})-\{(\Delta+\alpha_{\|}\zeta_{\|})^2+8\alpha_{\perp}\zeta_{\perp}\}^{\frac{1}{2}}]$$
$$E_3 = \alpha_{\|}\zeta_{\|}x_3$$
$$E_4 = \alpha_{\|}\zeta_{\|}$$
$$E_5 = \tfrac{1}{2}[(\alpha_{\|}\zeta_{\|}+\Delta)+\{(\alpha_{\|}\zeta_{\|}-\Delta)^2+24\alpha_{\perp}^2\zeta_{\perp}^2\}^{\frac{1}{2}}]$$
$$E_6 = \alpha_{\|}\zeta_{\|}x_6$$
$$E_7 = \tfrac{1}{2}[(\Delta-\alpha_{\|}\zeta_{\|})+\{(\Delta+\alpha_{\|}\zeta_{\|})^2+8\alpha_{\perp}^2\zeta_{\perp}^2\}^{\frac{1}{2}}]$$
$$E_8 = -2\alpha_{\|}\zeta_{\|}$$

where x_j's ($j = 1, 3, 6$) are the roots of cubic equation

$$x^3-(2+\eta)x^2+(2\eta-5\rho^2)x+6\rho^2 = 0\ ,$$

here $$\rho = \frac{\alpha_{\perp}\zeta_{\perp}}{\alpha_{\|}\zeta_{\|}}\ ; \qquad \eta = \frac{\Delta}{\alpha_{\|}\zeta_{\|}}$$

and Δ is the trigonal field separation between the split components (a doublet and a singlet) of the triplet ${}^5T_{2g}$

The corresponding eigen states are :

$$\psi_0 = a_0|1, -1> + b_0|0, 0> + a_0|-1, 1>$$
$$\psi_1 = a_1|1, 0> + b_1|0, 1> + c_1|-1, 2>$$
$$\psi_{-1} = a_1|-1, 0> + b_1|0, -1> + c_1|1, -2>$$
$$\psi_2 = b_2|1, 1> + a_2|0, 2>$$
$$\psi_{-2} = b_2|-1, -1> + a_2|0, 2>$$
$$\psi_3 = a_3|1, 0> + b_3|0, 1> + c_3|-1, 2>$$
$$\psi_{-3} = a_3|-1, 0> + b_3|0, -1> + c_3|1, -2>$$
$$\psi_4 = 1/\sqrt{2}|1, -1> - 1/\sqrt{2}|-1, 1>$$
$$\psi_5 = b_0/\sqrt{2}|1, -1> - \sqrt{2}a_0|0, 0> + b_0/\sqrt{2}|-1, 1>$$
$$\psi_6 = a_6|1, 0> + b_6|0, -1> + c_6|-1, 2>$$
$$\psi_{-6} = a_6|-1, 0> + b_0|0, -1> + c_6|1, -2>$$
$$\psi_7 = a_2|1, 1> - b_2|0, 2>$$
$$\psi_{-7} = a_2|-1, -1> - b_2|0, -2>$$
$$\psi_8 = |1, 2>$$
$$\psi_{-8} = |-1, -2>$$

where

$$a_0 = \frac{\sqrt{3}\,\alpha_1\,\zeta_1}{(\alpha_\parallel\,\zeta_\parallel - E_0)}\,b_0\,; \qquad 2a_0^2 + b_0^2 = 1$$

$$a_j = -\frac{\sqrt{3}(2\alpha_\parallel\zeta_\parallel - E_j)}{\sqrt{2}E}\,, \qquad a_j^2 + b_j^2 + c_j^2 = 1$$

$$b_j = \frac{2\alpha_\parallel\,\zeta_\parallel - E_j}{\sqrt{2}\alpha_1\,\zeta_j}\,c_j\,; \qquad j = 1, 3, 6$$

and $$a_2 = \frac{\sqrt{2}\alpha_1\,\zeta_1}{\Delta - E_2}\,b_2\,; \qquad a_2^2 + b_2^2 = 1$$

On these fine structure energy levels we apply the magnetic perturbation $[\beta H_x(-\alpha_1\,l'_x + 2S_x) + \beta H_y(-\alpha_1\,l'_y + 2S_y) + \beta H_z(-\alpha_\parallel l'_z + 2S_z)]$ to get the expressions for magnetic susceptibilities. If we then expand the energy in powers of the field strength H, we get,

$$W = W_i^{(0)} + W_i^{(1)}H + W_i^{(2)}H^2 + \ldots,$$

where the first term is the unperturbed energy, the second and the third terms are the first-order and second order Zeeman energy terms, respectively. Then,

the magnetic susceptibility upto the second order is given by (Van Vleck 1932),

$$K_p = N \frac{\sum_i [W_i^{(1)2}/kT - 2W_i^{(2)}] \exp(-W_i^{(0)}/kT)}{\sum_i \exp(-W_i^{(0)}/kT)}, \quad (p = \| \text{ or } \perp)$$

where N is the Avogadro number and k is the Boltzmann constant.

Final expressions for $K_\|$ and $K_\perp$ have been given by Bose & Rai (1965) The expressions being very lengthy, we do not present them again here.

Comparison of the Experimental Results with Theory and Discussions

The mean susceptibility and anisotropy of some of the Fe^{2+} salts measured by different authors are given below for comparison

Table 1

Salts	Temp °K	$\bar{K} \times 10^6$	$\Delta K \times 10^6$	
[1]$Fe(NH_4SO_4)_2.6H_2O$	300	12080	2620	$(K_\| > K_\perp)$
	100	36380	22040	
[2]$Fe(KSO_4)_2.6H_2O$	300	11790	3913	$(K_\| > K_\perp)$
	100	35980	24470	
*$FeSiF_6.6H_2O$	300	12470	2854	$(K_\perp > K_\|)$
	100	38800	14570	
[3][4](Fe, Mn)WO_4	300	11150	2430	$(K_\perp > K_\|)$
	100	32625	10940	

[1]Mukhopadhyay *et al* (to be published); *Mazumdar, 1966; [3][4]Present author.

It will be seen that for the first and third crystals the anisotropies are of same sign to the present case and the order of $\bar{K}$ is also the same indicating similar ligand fields in them The experimental anisotropy and susceptibility of Fe^{2+} ion (of wolframite) are compared with the theoretically computed values in table 2.

In theoretical computation we have derived by trial and error a set of values for $\alpha_\| k_\|$, $\alpha_\perp k_\perp$, $\alpha_\| \zeta_\|$, $\alpha_\perp \zeta_\perp$ and Δ, which gives the best fit with both the anisotropy and the susceptibility data, assuming that the first four parameters are independent of temperature. This is true for the absolute values to a good degree of approximation since the predominant cubic field mainly arises from the nearest strongly bound neighbours, but the anisotropy in α's k's and ζ's may be dependent on temperature in the same way as Δ Since the explicit relation between these anisotropic factors are not known, to avoid too many temperature dependent parameters, we throw the entire burden of the thermal dependence on Δ which may then cause this effect to be somewhat exaggerated. Our main purpose,

however, is to show the rough magnitude of this dependence hence we are justified in taking Δ as the only variable with temperature.

In our case Δ is negative. If we take Δ as positive the doublet $|\pm 1>$ occupy the lowest position giving $g_{\parallel} > g_{\perp}$ ($g_{\perp} \approx 0$) which implies $K_{\parallel} > K_{\perp}$. But our magnetic measurement definitely shows that $K_{\perp} > K_{\parallel}$; also we failed to fit the susceptibility and anisotropy data simultaneously, with any reasonable values of the parameters if Δ is taken as positive. Hence, we have fitted the experimental data with Δ negative which is consistent with the case of trigonally distorted $FeSiF_6$, $6H_2O$ (Bose & Rai, 1965) With Δ negative, the singlet E_0 lies lowest. Moreover, the energy levels E_i, $i = 0, 1, 2, \ldots 8$, follow the sequence in order of increasing values as calculated from our results given in table 3, agreeing with the sequence reported by Eicher (1963).

Table 2. Comparison of the theoretical and experimental values of $(K_{\perp} - K_{\parallel})$ and $\bar{K}$ with :

$\alpha_{\perp} k_{\perp} = 0.8$, $\quad \alpha_{\perp} \zeta_{\perp} = -80\ cm^{-1}$
$\alpha_{\parallel} k_{\parallel} = 0.7$, $\quad \alpha_{\parallel} \zeta_{\parallel} = -77\ cm^{-1}$.

Temperature °K	$-\Delta$ (cm^{-1})	$(K_{\perp} - K_{\parallel}) \times 10^6$	$\bar{K} \times 10^6$
90	950	12960 (12900)	36523 (36350)
100	960	10997 (10940)	32879 (32625)
150	925	6135 (6100)	22084 (21914)
200	890	4186 (4150)	16654 (16567)
250	850	3097 (3080)	13402 (13308)
300	800	2436 (2430)	11208 (11150)
400	700	1466 (1455)	8493 (8427)
500	580	877 (872)	6812 (6789)
600	450	489 (485)	5647 (5629)
700	300	268 (265)	4834 (4800)

The values in the parenthesis are the experimental values.

Δ is found to vary with temperature *e.g.*, $\Delta = 950\ cm^{-1}$ at 90°K to $\Delta = 300\ cm^{-1}$ at 700°K. We find that unless Δ is varied with temperature the agreement of theoretical wih experimental values at all but one temperature is poor with any

reasonable single set of parameters. The variation of Δ with temperature is possibly connected with the change in the strength of the crystal field with temperature, which is also corroborated by the variation of θ and ϕ with temperature, indicating rotation of the magnetic ellipsoid in the crystal.

Table 3. Energy of the ligand field levels in cm^{-1}

Temp. in °K	E_0	E_1	E_2	E_3				E_7	E_8
90	−950	−992.0	−984.9	−962 3	−140.3	−77 0	−35 0	21.3	89 3	154 0
300	−800	−849.7	−841 4	−814.4	−137.9	−77.0	−27.3	25.3	91.4	154.0
700	−300	−414.0	−400.0	−331.3	−117.1	−77.0	37.0	63.1	108 6	154.0

The variation of Δ (from 90°K to 700°K) is about 68%. This large variation of Δ as already mentioned is perhaps somewhat exaggerated and can be perceptibly reduced by varying α's, k's and ζ's with temperature, but then there will be too many parameters for unique solution of their values from the limited experimental data.

Table 1 shows that θ changes by about 15° while ϕ changes by about 3° only within the range of temperature from 90°K to 700°K. This shows that the ions rotate appreciably about an axis approximately parallel to the b-axis of the crystal as the temperature changes. A rotation of the ion about an axis parallel to b-axis will not be reflected in the values of ϕ, but it will manifest itself appreciably in the value of θ. This rotation affects the packing of the lattice with consequent changes in the anisotropic part of the ligand field with temperature.

The values of the parameters (Δ, $\alpha_{\|}k_{\|}$, $\alpha_{\perp}k_{\perp}$, $\alpha_{\|}\zeta_{\|}$, $\alpha_{\perp}\zeta_{\perp}$) in table 4 are of the expected order of magnitude as observed in other bivalent iron salts.

Table 4. Comparison of the field parameters of different salts.

Salts	Δ cm^{-1} at 300°K	100°K	$\alpha_{\|}k_{\|}$	$\alpha_{\perp}k_{\perp}$	$\alpha_{\|}\zeta_{\|}$ cm^{-1}	$\alpha_{\perp}\zeta_{\perp}$ cm^{-1}
$Fe(NH_4SO_4)_2.6H_2O$	−400		0.9	0.9	−80	−80
$Fe(KSO_4)_2.6H_2O$	660	260	0.8	0.7	−88	−80
$FeSiF_6.6H_2O$	−685	−815	0.8	0.8	−87	−90
(Fe, Mn)WO_4	−800	−950	0.7	0.8	−77	−80

By comparison of the above values it is apparent that the axial field (tetragonal) splitting in the second Tutton salt is of opposite sign to our case, also the variations

with temperature are different in the same range The other parameters are not very different showing that the covalency effect is more or less the same. The several parameters in the fluosilicate (trigonal distortion) compare very well with the present case in magnitude (also in sign for Δ) as is to be expected. Thus in spite of the very different structure of the two crystals, the ligand fields and the magnetic behaviours are in good general agreement. The values of $\alpha_{\|}$ & $\alpha_{\perp}$ in the case of trigonally distorted Fe^{2+} ion is expected to deviate from unity somewhat more than in the tetragonal case However, we cannot exactly evaluate $\alpha_{\|}$ & $\alpha_{\perp}$ in our case. Under the circumstances, taking them approximately equal to unity, the spin-orbit coupling coefficient comes out as reduced on the average by about 23% from its free ion value -103 cm^{-1}, due to overlap of the central $3d$ charge cloud with the surrounding s and p-charge clouds of the ligand oxygen atoms The overlap is likely to be anisotropic; hence the reductions in the spin-orbit coupling and the effective orbital factor are taken to be anisotropic in comparing the experimental data.

g-values The lowest level E_0 is singlet, followed by the doublet E_1, ~ 10 cm^{-1} higher up. The expressions for g-values are as follows :

$$g_{\|} = \{(4+\alpha_{\|}k_{\|})c_1^2+2b_1^2-\alpha_{\|}k_{\|}a_1^2\}$$

$$g_{\perp} = \{2\sqrt{3}a_1a_0-\alpha_{\perp}k_{\perp}(a_1b_0+b_1a_0)+2\sqrt{3}b_1b_0+2\sqrt{2}c_1a_0\}$$

No experimental reasonance data for $g_{\|}$ and $g_{\perp}$ on wolframite are available But from our magnetic susceptibility data at 300°K we can calculate $g_{\|}$ and $g_{\perp}$ as $g_{\|} = 2.0508$ and $g_{\perp} = 3.7527$. From these values the calculated mean g-value comes out as 3.285 which may be compared with the mean g value of Low's result, $g = 3.42$ (Low & Weger 1960) for Fe^{2+} ion embedded in MgO, in which the field has purely cubic symmetry, and with 2.99 calculated from the observed g-values ($g_{\|} = 8.97$, $g_{\perp} = 0$) for FeF_2 embedded in ZnF_2 (Tinkham, 1956), where Fe^{2+} ions have approximately tetragonal symmetry. The difference is quite appreciable and is to be expected in view of the different ligand fields in these crystals. g-values of $FeSiF_6$ calculated from magnetic susceptibility ($g_{\|} = 2.01$, $g_{\perp} = 3.76$, $\bar{g} = 3.30$, Bose and Rai, 1955, Mazumdar, 1966), where the symmetry of Fe^{2+} ions is trigonal, compare much better with the present crystal.

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